Sulfonated polystyrene pore-filled electrolytes membranes by electrons induced grafting of styrene into PTFE films : Thermal stability and structural investigation

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Abstract

The thermal stability and structural investigation of sulfonated polystyrene pore-filled electrolyte PTFE membranes prepared by radiation grafting of styrene into porous PTFE films and the subsequent sulfonation, were studied via using thermal gravimetric analysis and differential scanning calorimetry, respectively. A three-step degradation pattern was observed from TGA thermograms of all the membranes, which attributed to the dehydration, desulfonation, and degradation of the PTFE backbone. The weight losses in the membranes were found to be reliant on the grafting yield, whilst the degradation temperatures were shown to be independent of the grafting yield. The intrinsic crystallinity of the PTFE matrix was found to exhibit a decreasing trend with increasing in the grafting yield. A further decrease in crystalilinity was also observed in the sulfonation reaction. The residual crystallinity of the PTFE matrix approximately 11% was still remained in the membranes even after subjected to severe reaction conditions. The decreased in crystallinity of the resulting membranes can be explained by the combination of the dilution effect and the crystal disruption which occurred within the membranes matrix.

Keywords : pore-filled membranes; porous PTFE films; thermal stability; structural investigation;

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1. Introduction

There is considerable interest currently in the development of pore-filled electrolyte membranes for various applications [1,2,3]. These membranes have a variety of potential applications in pervaporation [4,5], temperature and pH (ionic strength) sensors [2], dialysis [6], proton exchange membrane [3,7] and so on. Efforts have been made in order to study and correlate the performance of such membranes with the grafting yield in these systems. The various steps which involved during the membranes preparation process is predicted to influence the overall structure of the membranes that depends upon the nature, amount and distribution of the grafted components [8].

The preparation of pore-filled electrolyte membranes for the fuel cell applications has been investigated by several researchers recently [3,7,9]. However, an extensive study to investigate the influence of the grafting upon the thermal stability as well as the structural changes in the resulting membranes has not widely studied. We have previously reported the preparation of proton exchange membrane by simultaneous radiation grafting after saturating the membranes pores with styrene monomer and subsequent sulfonation of the grafted films in order to yield sulfonated polystyrene pore-filled electrolyte PTFE membranes [10].

The introduction of the polystyrene grafts and of the hydrophilic sulfonic acid groups into the hydrophobic PTFE matrix produces a very complex structure, which has different natures (hydrocarbon and ionic group) from the pristine (fluorocarbon) matrix. Thus, in this paper we study the influence of the grafting yield and also the membrane preparation procedures on the thermal degradation and structure properties of the sulfonated polystyrene pore-filled electrolyte PTFE membranes, which were prepared by the simultaneous grafting method and followed by a sulfonation reaction have been studied.

2. Experimental

2.1. Materials and methods

The sulfonated pore-filled PTFE membranes were prepared by the simultaneous method. The materials, such as monomer (styrene) and polymer substrate (PTFE film: 150μm thickness, density of 1.94g/cm^3, average pore size of 0.15μm) and the grafting and sulfonation procedures were described in detail in the previous study [10]. The other chemicals were reagent grade and used without further purification.

2.2. Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis was carried out in order to study the thermal stability in term of the weight loss of the membranes samples during the experiment. The changes of weight throughout the TGA runs indicate the structure changes in the membranes. The TGA studies on membranes were carried out using Perkin-Elmer TGA-6. The membrane samples were initially dried under vacuum at 60^{o}C for 24 hrs and stored in a dessicator over silica gel. The samples were typically used 10 – 20 mg for the measurements. Analysis was carried out at a constant heating rate of 10.00°C/min under N_2 atmosphere in the temperature range of 50-700^{o}C for PTFE samples.

2.3. Differential scanning calorimetry (DSC)

Membranes with grafting yields in the range of (5.65% - 24.59%) were investigated for their thermal properties and structural changes in correlation with the

sulfonation process. Thermograms of samples were measured with a Mettler Toledo Star DSC instrument.

Prior to the DSC measurements, the sulfonated membrane samples were dried at 80^{o}C in vacuum oven (1 torr) for 7 days. The drying of the samples were necessary in order to eliminate the possible interference of moisture on the melting thermograms which is normally appear in the form of strong endothermic peak at 60 – 160^{o}C. After drying, the membranes were kept in a desiccator at ambient temperature over fresh silica gel. Typical samples having weight in the range of 5 – 10 mg were used. Pristine and grafted PTFE films were used as reference materials. The thermograms were studied in the temperature range of 50^{o}C – 400^{o}C for sulfonated PTFE membranes. The sulfonated PTFE samples were then cooled down to 50^{o}C after holding for 5 minutes isothermally at 400^{o}C. The heating rate during the runs was kept constant at 10^{o}Cmin^{-1} under nitrogen atmosphere. T_m was obtained from various points i.e. onset, the peak maximum and tail ends of the peak. The heat of fusion of the crystals was calculated from the peak area in the thermograms using Mettler Toledo Star system software.

The overall percentage crystallinity of the sample (Xc) was evaluated from the heat of fusion values of the corresponding membranes according to the following equation,

$$\text{Crystallinity} = \frac{\Delta H_{f(mem)}}{\Delta H_{f(crys)}} \times 100\% \qquad (2.1)$$

where $\Delta H_{f(mem)}$ is the heat of fusion measured for the membrane and $\Delta H_{f(crys)}$ is the heat of fusion for totally crystalline PTFE, which were taken as 92.9 J/g [11]. The heat of fusion values of the membranes $\Delta H_{f(mem)}$ were obtained from the area under the melting thermograms.

3. Results and discussion

Thermal stability is very important for membrane materials as it depends on its chemical and mechanical properties that in turn influence the overall performance of the membrane based system [12,13]. The thermal stability measurements of the sulfonated polystyrene pore-filled electrolyte PTFE membranes are performed via thermal gravimetric analysis (TGA) under nitrogen atmosphere at temperature range of 50 – 700^{o}C. The measurements included the pristine, grafted and sulfonated membranes in order to study the influence of the two preparation steps i.e., grafting and sulfonation, on the thermal stability of the pristine porous PTFE matrix.

TGA thermograms of pristine porous PTFE film, polystyrene pore-filled PTFE film having a grafting yield of about 24.59% and sulfonated polystyrene pore-filled electrolyte PTFE membrane having a grafting yield of about 24.59% are presented in Figure 1. It is observed that the pristine porous PTFE film remains stable up to 500^{o}C due to its perflourinated structure, which occurred with one-step decomposition as depicted in

thermogram “a”. The inclusion of polystyrene grafts into the PTFE backbone was found to undergo essentially two-step decomposition pattern (thermogram “b”). Empirically, the two components, PTFE and polystyrene, undergo fragmentation separately. The decomposition of polystyrene grafts starts at 400^{o}C and continues up to 470^{o}C, which left behind the more stable PTFE backbone decomposes at ~ 520^{o}C. This is in accordance with the view that the polystyrene grafts are incompatible with the PTFE matrix and form phase separated microdomains in the grafted polymer and behaved as a distinct two-phase system on thermal decomposition. Similar observations have been made by Gupta and Scherer.,[12], Nasef.,[14], Hietala et al.,[15] and Nasef et al.,[16] for the thermal decomposition of styrene grafted FEP, PTFE, PVDF and PFA films, respectively.

The sulfonation of the grafted film produced a strongly acidic polyelectrolyte membrane that will bring further alteration in the decomposition pattern of the membrane. The sulfonated membrane followed three-step decomposition as depicted from the three transitions revealed in thermogram “c”. In the first step, the weight loss starts below 100^{o}C and proceeds up to ~ 170^{o}C due to the loss of moisture present in the membrane during the preliminary heating. This is followed by a further two decomposition steps at ~ 350^{o}C and at ~ 530^{o}C, respectively. The weight loss in the second step is ascribed to the elimination of sulfonic acids groups from the membrane matrix and the final step is due to the decomposition of the PTFE backbone. It is intricate to have clear differentiation between the desulfonation and the decomposition of polystyrene chains in the sulfonated membrane because of the continuous weight loss in the range of 350^{o}C – 510^{o}C. These observations suggest that the sulfonated membrane make the membrane more susceptible toward thermal decomposition than the nonsulfonated membrane. Similar conclusions were drawn for polystyrene sulfonic acid membranes, which is based on PVDF [15], FEP [12,13], PTFE [14] and PFA [16] films. Based on the aforementioned results, it may be avowed that the membrane is thermally stable up to ~350^{o}C under the present experimental conditions.

The TGA thermograms for sulfonated polystyrene pore-filled electrolyte PTFE membranes with various grafting yield are shown in Figure 2. All of the membranes showed multi-step decomposition pattern that are attributed to the dehydration, desulfonation, decomposition of the polystyrene grafts and the decomposition of the PTFE backbone. It is observed that the membranes do not undergo complete decomposition in contrast to nonsulfonated membranes. Moreover, some of the residue is left behind at the end of the thermogram.

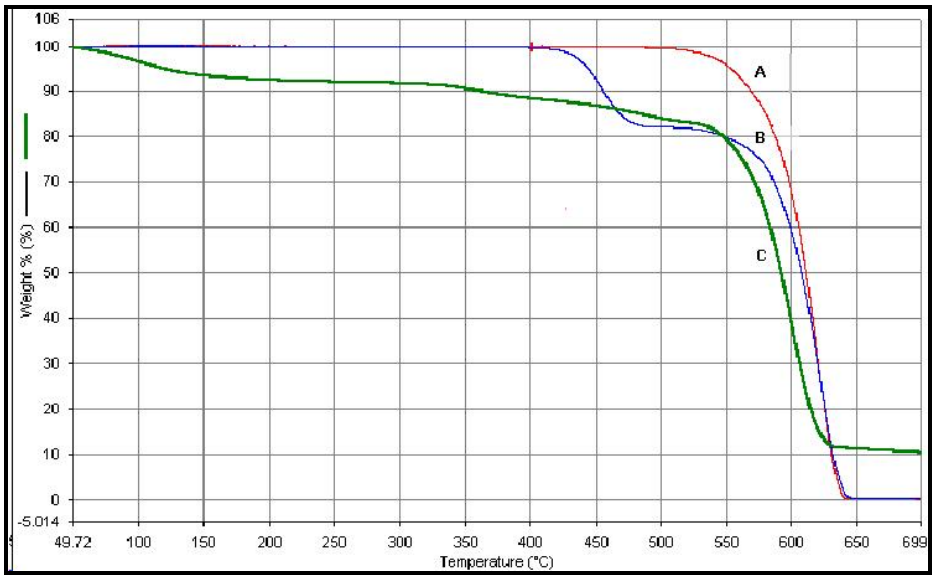

Figure 1: TGA thermogram of (A) pristine porous PTFE film; (B) polystyrene pore-filled PTFE film, grafting yield of 24.59% and (C) sulfonated polystyrene pore-filled electrolyte PTFE membrane, grafting yield of 24.59%.

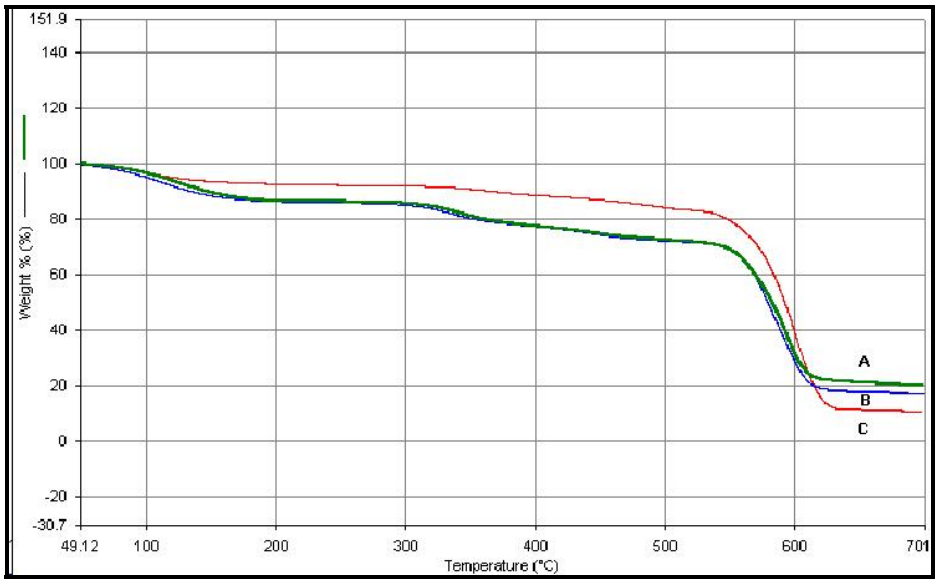

Figure 2: TGA thermogram of sulfonated polystyrene pore-filled electrolyte PTFE membranes having various grafting yields (A) 24.59%; (B) 15.96% and (C) 5.65%.

It is found that the residual weight percentage formed increases with the increase in the membranes grafting yield. This assumption is supported by the data obtained in Table 1 that illustrates the variation in residual weight percentage as a function of grafting yield after completing TGA run. These results suggested that the incorporation of sulfonic acid

groups encourages a propensity to the residual formation in the membrane and this propensity increases with the increase in the grafting yield. Hence, such behaviors indicated that the sulfonic acid groups play a vital role during the decomposition of the membrane which leads to the matrix thermally stable structure formation and becomes a factor to the residual formation at the end of the thermogram. These results are in a good agreement with those reported for styrene grafted and sulfonated PVDF [15], FEP [12,13], PTFE [14] and PFA [16] membranes.

The thermal and structural behaviors of the pristine porous PTFE film, the grafted film (polystyrene pore-filled PTFE film) and sulfonated membrane (sulfonated polystyrene pore-filled electrolyte PTFE membrane), respectively, were studied by differential scanning calorimetry. The melting thermograms of pristine PTFE film, grafted film and sulfonated membranes with various grafting yields in the range of 5.65% to 24.59% are depicted in Figure 3. Significant increase in T_m is found as the grafting yield is increased. This increasing trend is due to the incorporation of more amorphous polystyrene grafts that increase the amorphous fraction, which led to the reduction in the membranes crystallinity. Furthermore, the presence of bimodal melting endotherm is also observed after the pristine films are being grafted and sulfonated as shows in Figure 1-B, C, D, E which is due to the formation of crystallites having two different lamellae thickness. The form of the endotherm differs slightly after the grafted film is being sulfonated. The intensity of the bimodal melting peak for sulfonated membranes is substantially reduced in relation to the grafted film under the influence of sulfonation of polystyrene grafts. The size of these melting endotherms as well as the heat of melting (ΔHm) that obtained from the area under the melting peak decreases with increasing grafting yield.

Table 1
Variation of the sulfonated polystyrene pore-filled electrolyte PTFE membrane residue with the grafting yield after a complete TGA heating run (700^{o}C)

Grafting Yield (%)	**Weight of Residue (%)**
5.65	10.31
15.96	16.86
24.59	19.63

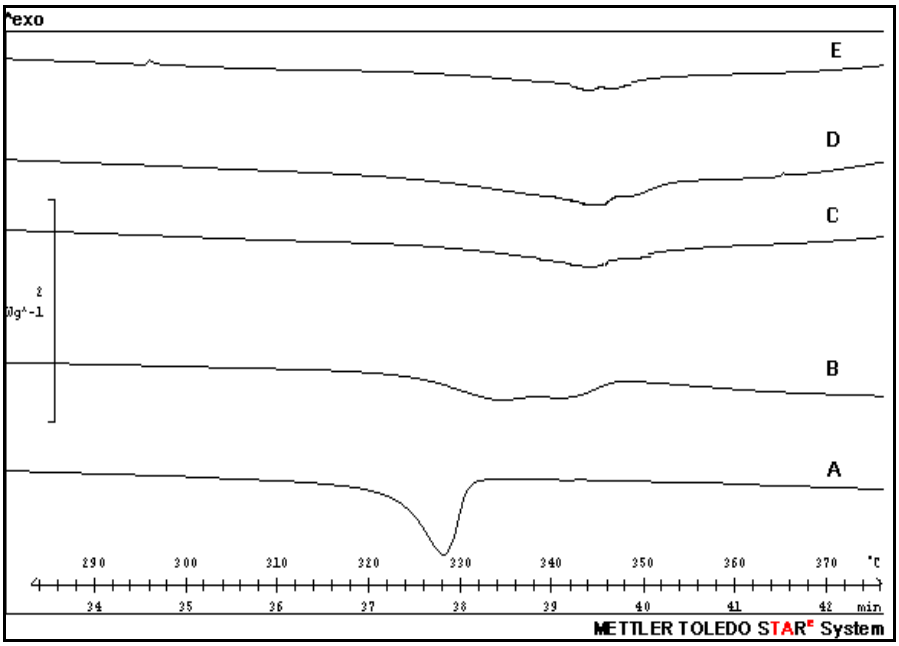

Figure 3: Melting thermograms of pristine porous PTFE film (A), 5.65% grafted PTFE film (polystyrene pore-filled PTFE film) (B) and sulfonated membranes (sulfonated polystyrene pore-filled electrolyte PTFE membrane) with various grafting yields of: (C) 5.65%; (D) 15.96%; (E) 24.59%.

The cooling thermograms of pristine porous PTFE film, grafted film (polystyrene pore-filled PTFE film) and sulfonated membranes (sulfonated polystyrene pore-filled electrolyte PTFE membranes) are presented in Figure 4. It is evident from Figure 4 that the crystallization of sulfonated membranes occurs at lower temperatures than in pristine and grafted films. The crystallization temperature decreases slightly with increasing grafting yields that is presumed due to the restrictive impact of the sulfonated polystyrene grafts on the mobility and ability to crystallize of the pristine PTFE matrix. This observation is well in agreement with the studies of Hietala et al., [17] on the structural investigation of radiation grafted and sulfonated PVDF membranes.

The crystallinity of the pristine and grafted films is approximately 35% and 28%, respectively. Further decreasing trend can be observed for the sulfonated membranes with increasing grafting yields as summarized in Table 2. These behaviors can be attributed to the dilution effect with the amorphous polystyrene grafts that took place in the membranes pores and the non-crystalline (amorphous) region of pristine film. Moreover, sulfonation of the grafted films is found to bring a further variation in the overall structural characteristics of the membranes. Crystallites disruption occurred as a result from the strong interaction between the hydrophilic sulfonic acid groups and the hydrophobic PTFE matrix. This results is in accord with the results reported by Gupta et al.,[8], Hietala et al.,[18] and Nasef[11], who also observed the relatively same phenomenon for styrene grafted and sulfonated FEP, PVDF and PTFE membranes, correspondingly. Hence, it can be concluded that the membrane two-step preparation procedure i.e grafting

and sulfonation was found to affect the thermal and structural properties (i.e T_m and crystallinity) of the resulting membranes that shifted to higher and lower values, respectively.

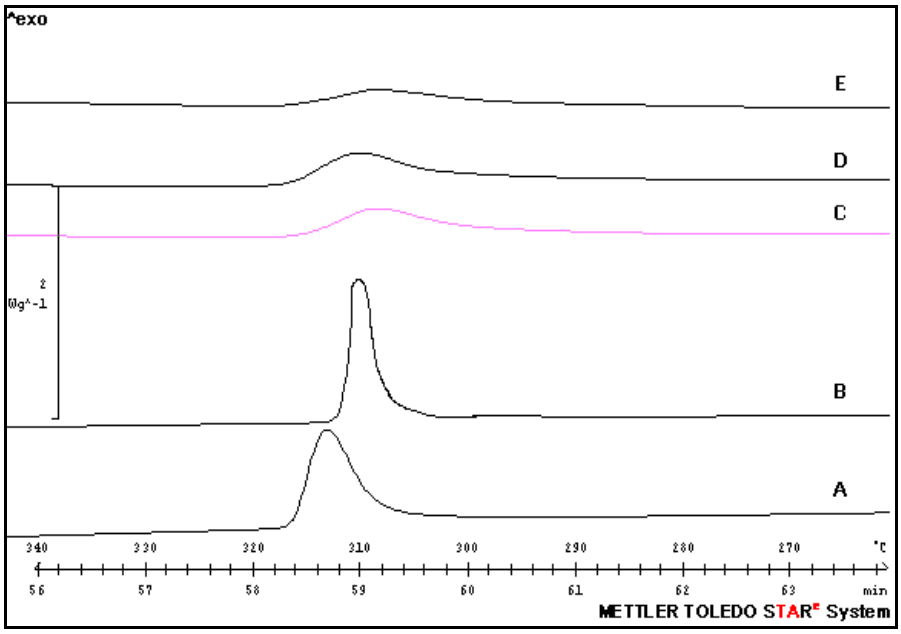

Figure 4: Cooling thermograms of pristine porous PTFE film (A), 5.65% grafted PTFE film (polystyrene pore-filled PTFE film) (B) and sulfonated membranes (sulfonated polystyrene pore-filled electrolyte PTFE membrane) membranes with various grafting yields of: (C) 5.65%; (D) 15.96%; (E) 24.59%.

Table 2
Thermal and structural properties of pristine, grafted (polystyrene pore-filled PTFE film) and sulfonated PTFE membranes (sulfonated polystyrene pore-filled electrolyte PTFE membranes) with various grafting yields.

Membrane	Melting Temperature (^oC)	Crystallization Temperature (^oC)	Crystallinity (%)
Pristine PTFE film	327.30	313.60	34.68
5.65% grafted PTFE film	335.00	310.00	28.33
5.65% sulfonated PTFE membrane	344.20	308.50	21.32
15.96% sulfonated PTFE membrane	346.00	310.50	21.02
24.59% sulfonated PTFE membrane	344.00	308.70	11.75

4. Conclusion

Proton exchange membranes have been successfully prepared via electron beam radiation grafting and subsequent sulfonation after saturating the pores of porous PTFE films with styrene monomers. The results showed that the properties of the membranes strongly depend on the grafting yield and the two-step membrane preparation procedures i.e. grafting and sulfonation.

The sulfonated polystyrene pore-filled electrolyte PTFE membranes were observed to have a thermal stability up to approximately 350^{o}C in nitrogen atmosphere. It was also found that these membranes showed a multi-step degradation pattern in a sequence of dehydration, desulfonation, and degradation of the PTFE backbone. The presence of polystyrene grafts in the PTFE matrix does not affect much alteration to the inherent degradation of the pristine film. This behavior indicates the incompatibility of the polystyrene grafts with the PTFE matrix and leads to the formation of a phase separated microdomains in the grafted film. The sulfonation of the grafted film produced a strongly acidic polyelectrolyte membrane (sulfonated polystyrene pore-filled electrolyte PTFE membranes) that brings further alteration in the decomposition pattern. The introduction of the strong hydrophilic sulfonic acid groups in the membrane during the sulfonation process makes it hygroscopic and also increases the membrane's susceptibily to thermal degradation in contrast to the pristine and grafted PTFE films.

The structural studies of sulfonated polystyrene pore-filled electrolyte PTFE membranes reveal that the crystallinity of the PTFE matrix has decreased upon both grafting and sulfonation reactions as well as the variation of grafting yield. The decrease in crystallinity of the resulting membranes is probably caused by the combination of the dilution effect and the crystal disruption. This dilution effect is formed from the incorporation of grafted amorphous polystyrene grafts at the non-crystalline region and pores of the PTFE matrix, which increase gradually with the grafting yields. Meanwhile, the crystallites disruption takes place probably due to the strong interaction between the hydrophilic sulfonic acid groups and the hydrophobic PTFE matrix under the influence of the sulfonation of polystyrene grafts.

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